5 The effect of the ancillary ligand on catalyst performance of [η^5-C_5H_3R-(B)-Ar]$TiCl_3$/MAO systems in selective ethene trimerization*

5.1 Introduction

Ligand effects in homogeneous metallocene catalysts (for olefin polymerization) have been discussed qualitatively as early as 1971, when Olivé and Henrici-Olivé pointed out that 'catalyst tailoring' by modification of the catalyst structure could lead to specific changes in catalytic activities and product properties[1]. Ligand variations in catalytic processes can affect the activity, the selectivity (i.e. chemo-, regio- and stereoselectivity), the stability and, in polymerization catalysis, the polymer molecular weight (chain propagation vs chain termination). Some representative examples from the field of olefin polymerization and oligomerization are given in the following paragraphs.

Activity: Ligand substituents can influence the activity of olefin polymerization catalysts via both steric (e.g. on cation-anion separation), and electronic effects (e.g. the electron density on the metal center)[2]. Frequently, a subtle interplay between steric and electronic effects of the various substituents determines the overall activity of the resulting catalyst, and it is often impossible to separate the steric and/or electronic factors that are responsible for this[3].

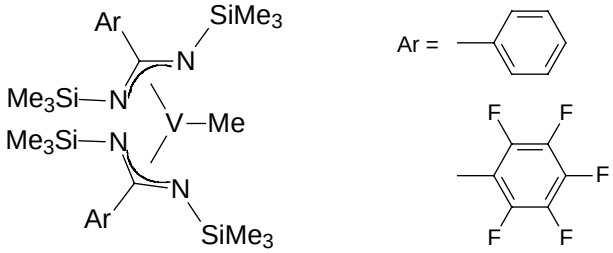

Figure 1: Benzamidinate vanadium(III) complexes for ethene oligomerization

A nice example in which the ligand substituent effect on catalyst activity can be rationalized, is in the catalytic ethene oligomerization (to give a Flory-Schulz distribution of linear α-olefins) with neutral bis(benzamidinate) vanadium(III) complexes, $[ArC(NSiMe_3)_2]_2VMe$ (Ar = C_6H_5, C_6F_5; Figure 1)[4]. In these neutral

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systems (no cation-anion interactions to take into account), the introduction of the electron-withdrawing C_6F_5 substituent on the backbone of the ancillary ligand (remote from the active site of the catalyst) improves the oligomerization activity by making the metal center more Lewis acidic and increasing the polarization of the V-alkyl bond.

Selectivity: The effect of substituents on the *stereo*selectivity in the polymerization of 1-alkenes have been most notably studied for isospecific C_2-symmetric *ansa*-metallocenes, for which the molecular microstructure of the resulting polymer strongly depends on the biscyclopentadienyl or bisindenyl-based ligand structure[5]. Experimental and theoretical studies have identified the substitution positions most relevant to catalyst performance (Figure 2).

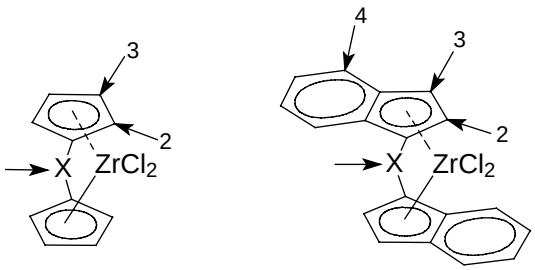


Figure 2: Substitution positions important for catalyst stereoselectivity

Bisindenyl 1,1'-*ansa*-zirconocenes with bridging moieties (X), preferably $SiMe_2$ (Figure 3), that enforce the rigidity of the ligand framework, and thus the retention of the C_2-symmetry in the *rac*-isomers, were found to improve the stereoselectivity of propene polymerizations[6]. Analogous metallocenes with different bridging moieties cannot rival the stereocontrol exerted by the former systems[7]. The introduction of substituents on the 2,2'-positions were calculated[8], and experimentally confirmed[9], to restrict the mobility of the ligand framework and, as a consequence, to improve the stereoselectivity (Figure 3). Additional substitution on the 4,4'-position leads to a further increase in stereoselectivity (Figure 3)[10]. Furthermore, the 4,4'-substituents significantly improve the *regio*selectivity of these systems by effectively guarding against a monomer orientation that would lead to 2,1 monomer insertion affording a slowly reacting chain end. As a result, they also display a very high *activity* and yield higher *molecular weight* polypropene.

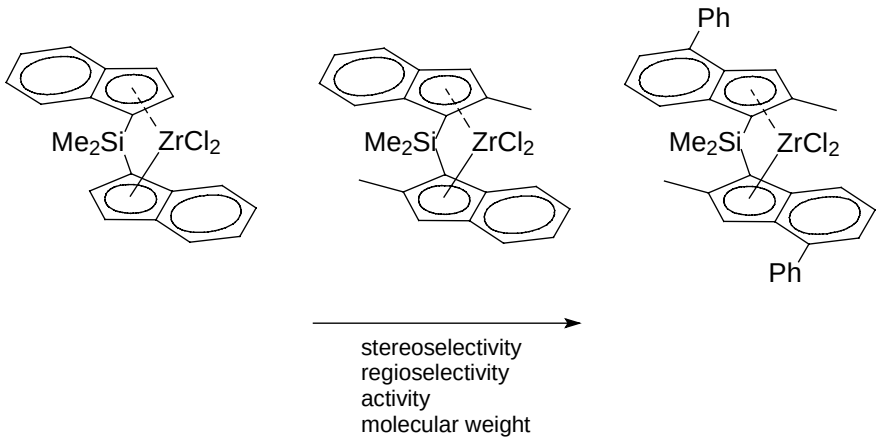


Figure 3: Ligand effects on catalysts performance in *ansa*-bisindenyl-metallocenes

Molecular weight: The molecular weight of a polymer is controlled by the relative rates of chain propagation and chain termination. The latter example illustrates that by increasing the rate of chain propagation (by avoiding 2,1-insertions that lead to slowly reacting secondary chain ends), the molecular weight of the resulting polymer increases accordingly. In chapter 1, we mentioned two catalyst systems (Figure 4) that can switch from oligomerization[11] (R = Me) to polymerization[12] (R = *i*-Pr) activity by introducing ligand substituents (in the axial positions) that effectively suppress the chain termination transition state, and thus decrease the rate of chain termination to give higher molecular weight products.

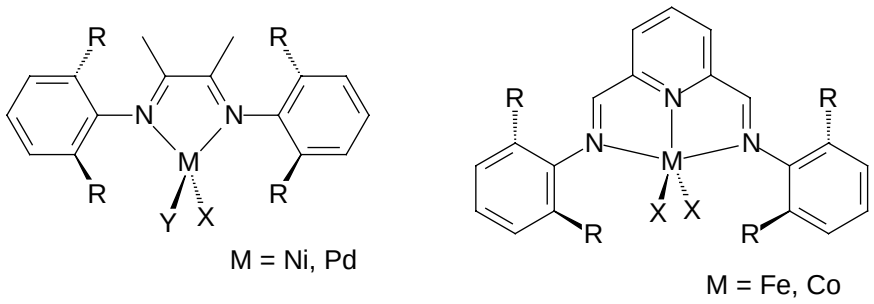


Figure 4: Polymerization/oligomerization catalysts

Similarly, sterically demanding fluorenyl ligands, which can be considered as substituted Cp ligands, were found to disfavor chain termination, and to allow the formation of (atactic) poly-1-hexene[13] (Flu_2ZrR_2) and polypropene[14] ($[Me_2Si(9\text{-}Flu)_2]ZrR_2$) with higher molecular weights as that produced with, for example, Cp_2ZrR_2[15].

Stability: In the previous chapter, we already described how tethered labile moieties in hemilabile ligands can stabilize catalytically active species[16] while retaining the catalytic activity, for example, in the $[(IndR)Ni(PPh_3)]^+$ system[17] (Scheme 5, Chapter

4). Substitution with non-coordinating moieties can also improve catalyst stability. For example, the thermal stability of $IndTiCl_3$ is better than that of $CpTiCl_3$ in styrene polymerization[18]. The introduction of ligand substituents can also influence, e.g. cation-anion (*vide supra*) or solvent interactions, which in turn can affect catalyst stability[19]. It should be taken into account that seemingly innocent ligand substituents may open deactivation pathways not available for unsubstituted or alternatively substituted ligand systems, and as a consequence diminish catalyst stability[20]. In our trimerization catalysts, deactivation of the catalytic species can potentially occur through *ortho* cyclometalation of the $[C_5H_4CMe_2Ar]^-$ ligands, as described in Chapter 2 and 3.

In the previous chapter, we described the selective ethene trimerization with (η^5-$C_5H_4CMe_2Ar)TiCl_3$/MAO, and proposed a mechanism for the trimerization. In our systems, some of the issues discussed in the foregoing part of this introduction are important, especially with respect to the selectivity for trimerization (C_6 and C_{10}) vs polymerization (PE). Also the C_6 vs C_{10} selectivity, and the distribution of products within these respective fractions are of interest, and insight into the way in which ligand variations can influence this can help us to understand these intriguing systems better. Additionally, the catalysts are clearly prone to deactivation, as indicated by the decrease in ethene consumption in time, and the poor thermal stability. In order to maximize the yield of trimer per g titanium it is necessary to understand the factors that govern the catalyst stability and activity. A fundamental study of the effect of ligand variations on the catalytic properties can provide information that may allow a rational improvement of catalyst performance.

5.2 Ligand effects in catalysis by half-sandwich titanium compounds

Besides the effect of chelating and potentially labile groups (see section 3.2 and 4.3), the effect of non-chelating substituted cyclopentadienyls on the syndioselectivity and activity of styrene polymerization by half-sandwich titanium compounds has been investigated. Chien and Rausch reported the effect of methyl, diphenylphosphino and trimethylsilyl substituents in monocyclopentadienyl titanium trialkoxide/MAO catalysts[21]. The introduction of one methyl group to give (η^5-$C_5H_4Me)Ti(OR)_3$ afforded a catalyst with better activity and selectivity than the reference system $CpTi(OR)_3$. The other two substituents led either to diminished activity or selectivity, or both (these effects have not been rationalized in terms of steric and electronic factors). Replacing the cyclopentadienyl group by an indenyl increases the activity, stereospecificity and the thermal stability of the catalyst[18]. Small electron-releasing substituents on the indenyl ligand, preferably a methyl group, were found to improve catalyst performance, whereas bulky substituents, Lewis basic groups[22] or additional methyl groups[23] reduced catalytic activity. The introduction of a phenyl substituent or an annelated aromatic group on the indenyl ligand, e.g. benz[*e*]indenyl, were found to enhance catalyst performance, supposedly

due to delocalization of the negative charge of the indenyl ligand in the aromatic group[24]. A similar effect was observed for the catalyst precursor [η^5-$C_5H_4(C_6F_5)$]$TiCl_3$, which shows improved catalyst performance in styrene polymerization (higher activity, higher syndioselectivity, and higher T_m), reportedly due to the electron-withdrawing properties of the C_6F_5 group[25].

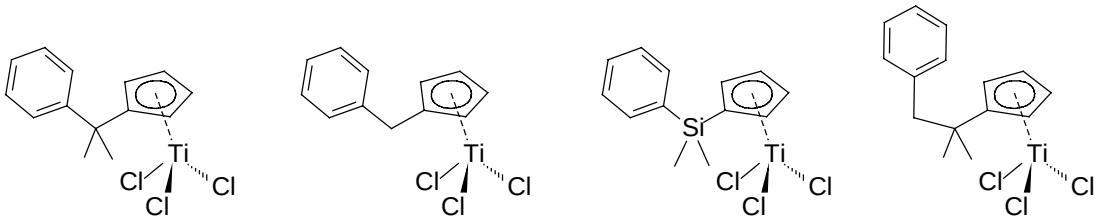
In this chapter, we investigate and discuss the effect of variations in the bridging moiety, cyclopentadienyl substituents, and combinations of these (and substitutions on the aryl moiety, which have been described in Chapter 4) on the activity, selectivity and stability of [η^5-(3-R)C_5H_3-(B)-Ar]$TiCl_3$/MAO catalysts. We show that easily accessible ligand variations can lead to increased trimerization activity (by up to 92%), and to catalysts with a greatly improved active lifetime.

5.3 Effect of the bridge between the cyclopentadienyl and arene group

In order to probe structure-performance relationships in the [$C_5H_4CMe_2Ar$]-based selective ethene trimerization catalyst systems, the effect of the bridge between the cyclopentadienyl ligand and the arene group on catalytic ethene conversion was investigated. The precatalysts (η^5-$C_5H_4CH_2Ph$)$TiCl_3$ (**26**), (η^5-$C_5H_4SiMe_2Ph$)$TiCl_3$ (**27**), and (η^5-$C_5H_4CMe_2CH_2Ph$)$TiCl_3$ (**28**) were tested in ethene conversion with MAO activator, and compared with the reference catalyst (η^5-$C_5H_4CMe_2Ph$)$TiCl_3$ (**1**)/MAO. The results are listed in Table 1.

Table 1: Catalytic ethene conversions with the (η^5-C_5H_4-(B)-Ph)$TiCl_3$/MAO catalyst systems (toluene solvent, 5 bar ethene, 30 °C, 15 µmol Ti, Al:Ti = 1000, 30 min reaction time)

Catalyst (B)	C_6 products [g] (wt%)	C_8 products [g] (wt%)	C_{10} products [g] (wt%)	C_{12-24} products [g] (wt%)	PE [g] (wt%)	Trimerization products [wt%]
1 (CMe_2)	20.9 (83)	0.3 (1)	3.5 (14)	0.1 (0.5)	0.5 (2)	97
26 (CH_2)	2.7 (42)	0.4 (6)	0.6 (9)	0.6 (9)	2.2 (34)	<51
27 ($SiMe_2$)	2.1 (36)	0.3 (5)	0.4 (7)	0.5 (8)	2.6 (44)	<43
28 (CMe_2CH_2)	1.2 (83)	0.1 (7)	0.05 (3)	0.01 (0.7)	0.1 (7)	86



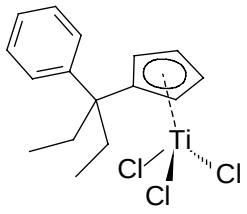
1 **26** **27** **28**

The catalysts with the CH_2 and $SiMe_2$ bridges (**26** and **27** respectively) both produce 1-hexene and polyethene in comparable amounts, together with a Flory-Schulz type distribution of higher 1-alkenes. These systems thus have a very poor selectivity for trimerization. The catalyst **28** produces mainly 1-hexene, but at a very slow rate. From the above experiments it is clear that a disubstituted C_1-bridge between the cyclopentadienyl and arene moieties gives the best selectivity and activity in catalytic ethene trimerization. To refine this point further, we prepared three more precatalysts of the type $[\eta^5\text{-}C_5H_4\text{-(B)-Ph}]TiCl_3$ that satisfy this requirement: **29** (B = CEt_2), **30** (B = $C[(CH_2)_5]$) and **31** (B = $C{=}CH_2$). The data in Table 2 show that, upon activation with MAO, all these catalysts are indeed active and selective in ethene trimerization. The performance of **30**/MAO, with the bridging carbon forming part of a 1,1-disubstituted cyclohexane moiety, even exceeds that of the catalyst **1**/MAO, whereas the catalyst with the CEt_2 bridge is somewhat inferior to its CMe_2 analogue in both activity and selectivity. Interestingly, the catalyst **31**/MAO, with an sp^2 bridging carbon, also performs reasonably well, with trimerization behavior comparable to that of the catalyst with the CEt_2 bridge.

Table 2: Catalytic ethene conversions with the $(\eta^5\text{-}C_5H_4CR_2Ph)TiCl_3$/MAO catalyst systems (toluene solvent, 5 bar ethene, 30 °C, 15 µmol Ti, Al:Ti = 1000, 30 min reaction time)

Catalyst (R_2)	C_6 products [g] (wt%)	C_{10} products [g] (wt%)	PE [g] (wt%)	Productivity C_6 products[a]	Trimerization products [wt%]	Trimerization productivity[b]
1 (Me_2)	20.9 (83)	3.5 (14)	0.5 (1.8)	555	97	109.5
29 (Et_2)	18.5 (88)	1.4 (7)	1.0 (4.6)	495	95	92.0
30 (-$(CH_2)_5$-)	24.4 (87)	2.9 (10)	0.6 (2.0)	650	97	124.5
31 (=CH_2)	17.3 (88)	1.4 (7)	0.9 (4.7)	460	95	86.5

[a] in g C_6 product per mmole Ti, bar and h; [b] in mole olefinic bonds trimerized per mmole Ti and h



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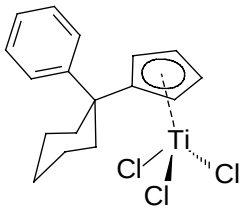

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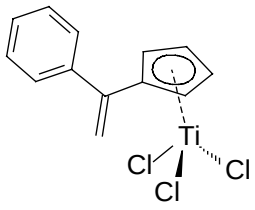

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From Table 1, it becomes clear that the bridging unit plays a crucial role in the selective ethene trimerization performance of these catalyst systems. The transformation of the catalyst from a species active in polymerization into one that is active in trimerization in the proposed mechanism (see section 4.7) involves the coordination of the arene moiety to the electron-deficient titanium center to generate

the *ansa*-Cp-arene Ti(II) species. Apparently, both the CH_2 (**26**) and $SiMe_2$ (**27**) bridged compounds are less effective in this respect than the CMe_2-bridged compound (**1**). It is as yet unclear whether this is the result of a slow switch from the polymerization catalyst (Ti(IV)-dialkyl) to the trimerization catalyst (Ti(II)/Ti(IV)-metallacycle), promoted by (intramolecular) arene coordination, or if the trimerization catalyst, once formed, can readily be transformed back into a species active in polymerization.

Catalyst precursors **1** and **26** have recently been compared in the polymerization of styrene[26]. The **1**/MAO (CMe_2-bridged) system displayed significantly lower polymerization activity and afforded syndiotactic polystyrene with a lower molecular weight and melting temperature than the CH_2-bridged catalyst **26**/MAO. The authors suggest that coordination of the phenyl group in **1** is enhanced relative to **26**, and that competetive complexation of the ancillary ligand phenyl group with the phenyl group of the last inserted styrene monomer[27] lowers the activity and retards chain propagation relative to chain termination, thus yielding lower molecular weight PS (see also section 3.2)[28]. Differing coordinating properties of the phenyl group in cationic metallocene species with $C_5H_4CR_2Ph$-ligands (R = H, Me) were also observed by Green and Bochmann. Activation of $(\eta^5\text{-}C_5H_4CR_2Ph)_2ZrMe_2$ with 1 equiv of $[Ph_3C][B(C_6F_5)_4]$ leads to the formation of the homobinuclear species $\{[(\eta^5\text{-}C_5H_4CR_2Ph)_2ZrMe]_2(\mu\text{-}Me)\}[B(C_6F_5)_4]$ for R = H[29], whereas for R = Me the monomeric $[(\eta^5\text{-}C_5H_4CR_2Ph)_2ZrMe][B(C_6F_5)_4]$ species is formed[30]. NMR spectroscopy of the latter tentatively suggests intramolecular coordination of the pendant phenyl group. The differences in behavior are explained by the increased steric bulk of the $C_5H_4CMe_2Ph$-ligand, with respect to $C_5H_4CH_2Ph$, the increased electron-donating properties of the arene moiety (due to the electron-donating methyl groups in the backbone), and the Cp-C-arene angle compression (Thorpe-Ingold effect[31]) by the backbone methyl groups, all which facilitate phenyl coordination to the cationic Zr center. These findings indicate that the formation of *ansa*-cyclopentadienyl-arene titanium cations, the prerequisite for selective ethene trimerization activity, is more facile and effective for the CMe_2-bridged species explaining the differences in ethene conversion for **1** and **26**/MAO. A negative effect of metal-arene interaction in metallocene species was proposed to explain the observation that in ethene polymerization with $[\eta^5\text{-}C_5H_4\text{-}(B)\text{-}Ph]_2ZrCl_2$/MAO systems (B = CH_2, CMe_2, $SiMe_2$), the CH_2 and $SiMe_2$-bridged species are about 20 times as active as the CMe_2-bridged species[2b].

The catalyst performance of the $SiMe_2$-bridged species **27** is most likely related to the poor accessibility of the *ansa*-Cp-arene coordination mode of the ancillary ligand. Due to the larger ionic radius of silicon (0.26 Å) versus carbon (0.15 Å)[32] the ligand has to adopt a much more acute Cp-C-arene bend angle to accommodate *ansa*-coordination. In the X-ray structures of $[Me_2X(\eta^5\text{-}C_5H_4)]ZrCl_2$ (X = C[33], Si[34]) a difference of 6.3° can be observed in the respective bend angles. In addition, Bochmann and coworkers reported that the reaction of $(\eta^5\text{-}C_5H_4SiMe_2Ph)TiMe_3$ with either $B(C_6F_5)_3$ or $[Ph_3C][B(C_6F_5)_4]$ affords highly thermally labile species (even at -

60 °C), in contrast to the readily characterized complex [(η^5,η^6-$C_5H_4CMe_2Ph$)$TiMe_2$][$B(C_6F_5)_4$], tentatively suggesting the absence of the crucial arene coordination in the former cationic species[35]. These observations may indicate a slow conversion from ethene polymerization to the selective trimerization active species in **27**/MAO (*vide supra*).

In the same study, Bochmann reported the clean formation of an *ansa*-cyclopentadienyl-arene cationic species for the reaction of the trimethyl derivative of **28**, (η^5-$C_5H_4CMe_2CH_2Ph$)$TiMe_3$, with $B(C_6F_5)_3$, and its moderate activity in propene polymerization. The closely related catalyst system (η^5-$C_5H_4CH_2CH_2Ph$)$TiCl_3$/MAO was tested in ethene polymerization and was found to show poor activity[36] (note that in this experiment the reaction solution was not analyzed for soluble products, so that any produced 1-hexene will have gone unnoticed). The latter catalyst displays high activity for the polymerization of styrene, which prompted the authors to conclude that there are no bonding interactions between the pendant phenyl group and the titanium center under catalysis conditions. Interestingly, the C_5Me_4-analog (η^5-$C_5Me_4CH_2CH_2Ph$)$TiCl_3$/MAO was previously found to show a strongly diminished styrene polymerization activity[28], attributed to coordination of the pendant arene. The relatively good trimerization selectivity of the **28**/MAO system (86%, albeit at a slow rate), and Bochmann's observations, suggest that *ansa*-cyclopentadienyl-arene coordination, crucial for trimerization selectivity, is accessible in the catalytically active species derived from **28**. The longer, more flexible CMe_2CH_2-bridge probably allows for a stronger η^6- arene coordination in **28** than for **1** with the CMe_2-bridge. For example, the X-ray structure of {[(η^5,η^6-$C_5H_4CMe_2$-3,5-$Me_2C_6H_3$)Ti(μ-Br)]$_2$}[$B(C_6F_5)_4$]$_2$ (**18**) indicates that the arene moiety does not coordinate in a fully symmetrical η^6-fashion, but that the three carbons closest to the bridge show shorter Ti-C distances than the other three (approaching η^3-coordination). The 'constrained geometry' of the C_1-bridged species might facilitate the 'ring slippage', proposed for the rate-determining insertion of the third ethene molecule into the titanacyclopentane, resulting in a higher trimerization activity for **1** with respect to **28**.

The effect of backbone substituents on catalyst performance is well-documented for CR_2-bridged *ansa*-metallocenes, for which it was found that bulky groups R such as phenyl or cyclohexyl improve polymerization activity and stereoselectivity[37]. The differences in trimerization activity between the **1**, **29** and **30**/MAO systems are relatively small (max. 25%), and can be the result of the different steric properties of the backbone substituents or other effects that influence the propensity for arene 'ring slippage' in the proposed rate-determining step. Since *ansa*-cyclopentadienyl-arene coordination of the ancillary ligand is crucial to ethene trimerization reactivity (*vide supra*), the behavior of the [$C_5H_4C(=CH_2)Ph$]-ligand (**31**) is somewhat puzzling. In order to adopt the necessary conformation, the theoretical Cp-C-arene bend angle in this ligand of 120° has to undergo a reduction of more than 20° (for the related species {[(η^5,η^6-$C_5H_4CMe_2$-3,5-$Me_2C_6H_3$)Ti(μ-Br)]$_2$}[$B(C_6F_5)_4$]$_2$ (**18**) the bend angle is 95.8°). For the $SiMe_2$-bridged species **27** a similar angle compression

was presumably insurmountable, resulting in low ethene trimerization selectivity. It might be that transient interaction of the olefinic group in the backbone[38] with titanium facilitates the formation of an *ansa*-cyclopentadienyl-arene titanium species, deemed crucial for transformation to ethene trimerization catalysis, although the conformational constraints of the ligand seem to preclude true η^2-coordination to the metal center.

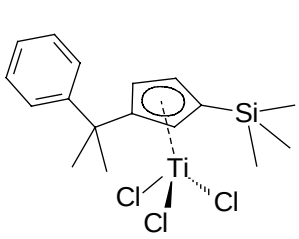
5.4 Effect of substituents on the cyclopentadienyl group

The effect of the attachment of substituents on the cyclopentadienyl moiety of the cyclopentadienyl-arene catalysts was probed by the synthesis of three precatalysts of the type $[\eta^5\text{-}(3\text{-R})C_5H_3CMe_2Ph]TiCl_3$: **32** (R = $SiMe_3$), **33** (R = CMe_3) and **34** (R = CMe_2Ph). The results of catalytic ethene conversion with these catalysts using MAO activator, and comparative data for the reference catalyst **1**/MAO, are listed in Table 3.

Table 3: Catalytic ethene conversions with the $[\eta^5\text{-}(3\text{-R})C_5H_3CMe_2Ph]TiCl_3$/MAO catalyst systems (toluene solvent, 5 bar ethene, 30 °C, 15 µmol Ti, Al:Ti = 1000)

Catalyst (R)	time [min]	C_6 products [g] (wt%)	C_{10} products [g] (wt%)	PE [g] (wt%)	Productivity C_6 products[a]	Trimerization products [wt%]	Trimerization productivity[b]
1 (H)	30	20.9 (83)	3.5 (14)	0.5 (1.8)	555	97	109.5
1 (H)	120	27.9 (78)	6.6 (18)	1.0 (2.8)	185	96	38.0
32 ($SiMe_3$)	30	25.2 (85)	3.3 (11)	0.4 (1.2)	670	96	129.5
33 (CMe_3)	30	14.7 (89)	0.9 (5)	0.7 (4.3)	390	94	72.5
34 (CMe_2Ph)	30	11.9 (91)	0.6 (5)	0.3 (2.3)	315	96	58.5
34 (CMe_2Ph)	120	46.6 (89)	4.1 (8)	0.8 (1.5)	310	97	58.5

[a] in g C_6 product per mmole Ti, bar and h; [b] in mole olefinic bonds trimerized per mmole Ti and h



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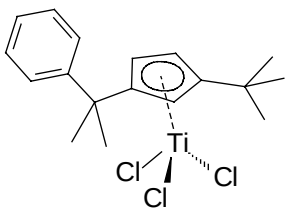

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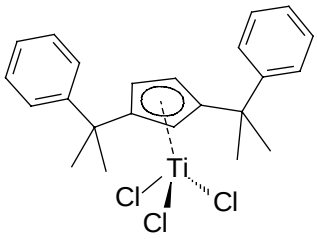

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As expected, all three systems show good selectivity for trimerization. The $SiMe_3$-substituted catalyst **32**/MAO shows a somewhat improved activity over **1**/MAO, but

the CMe_3-substituted catalyst **33**/MAO exhibits a lower productivity and selectivity over the 30 min run period. This appears to be due to a catalyst degradation process in the latter system. Its initial ethene uptake rate is comparable to that of **32**/MAO, but decreases much more rapidly in time, the catalyst being fully deactivated after 15 min. The catalyst **34**/MAO that has two CMe_2Ph substituents on the cyclopentadienyl ring, which, in principle, can both (alternately) coordinate to the metal center, is selective but rather slow compared to **1**/MAO. Nevertheless, catalyst **34**/MAO does have a very interesting feature. As mentioned before, the thermal stability of **1**/MAO is only modest, and even at 30°C catalyst degradation is taking place noticeably. The top two entries of Table 3 describe the behavior of **1**/MAO at run times of 30 and 120 min respectively. It is clear that catalyst deactivation limits the total turnover attainable by this catalyst to around 48 kg trimerization product per g Ti. In contrast, **34**/MAO displays an identical productivity (around 310 kg C_6 mol^{-1} h^{-1} bar^{-1}) over both the 30 min and 120 min runs, affording a total turnover of 71 kg trimerization product per g Ti after 120 min. Thus the presence of two CMe_2Ph substituents slows down the catalysis, but greatly improves catalyst stability. This may be related to our observation, mentioned earlier (section 4.6), that **1**/MAO degrades less rapidly in neat toluene solvent than in a *n*-octane/toluene (80:20) mixture, possibly indicating catalyst stabilization by transient toluene coordination.

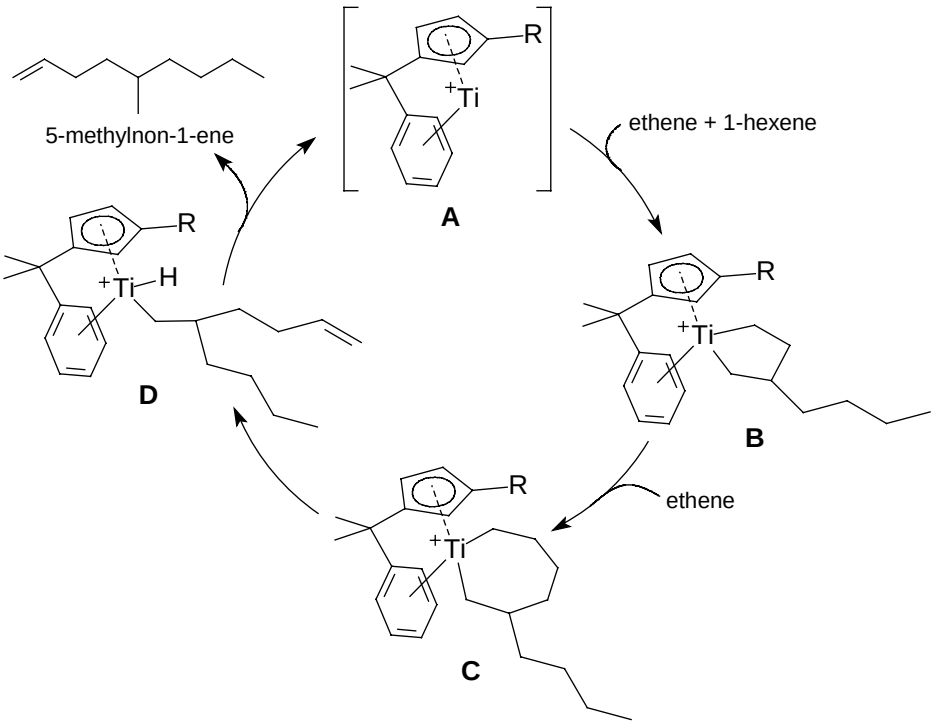
The stabilities of the catalysts **32** (R = $SiMe_3$) and **33** (R = CMe_3)/MAO differ significantly. The actual deactivation mechanism is not known presently, but various possible pathways can be suggested. For one, it is possible that electronic effects play a role in the stabilization of the catalytic species. The effect of $SiMe_3$ versus CMe_3 substituents in $(\eta^5\text{-}C_5H_4R)_2ZrCl_2$ systems has been the subject of fundamental (cyclic voltammetry[39], XPS[40]) and polymerization studies[41]. The CMe_3 group is an electron donor, and (despite some conflicting results[42]) the $SiMe_3$ group is generally considered to be electron-withdrawing[43]. As suggested earlier, (transient) arene coordination improves catalyst stability. The electron-donating *tert*-butyl group of **33** increases the electron density on the titanium center and leaves it less prone to arene coordination, and hence more amenable to catalyst deactivation. Following the same line of reasoning, the electron-withdrawing $SiMe_3$ group should enhance the stability of the **32**/MAO system. However, the rate of deactivation of the $SiMe_3$ substituted catalyst **32** and the unsubstituted catalyst **1** are similar, as can be seen from the ethene uptake profiles. The closely resembling initial ethene uptake rate for **32** and **33**/MAO does suggest that initial trimerization activity may be affected by steric factors (possibly on cation-anion separation).

A second potential deactivation pathway involves the cyclometalation of the arene moiety of the ancillary ligand. In chapter 3, we showed that in cationic cyclopentadienyl-arene titanium alkyl complexes cyclometalation of the arene by σ-bond metathesis is facilitated by alkyl ligands, such as benzyl groups, that can induce (partial) ligand-arene dissociation. A donor substituent on the cyclopentadienyl ligand, such as CMe_3, can perform a similar function by weakening the arene coordination to the metal center (*vide supra*). However, the almost perfect stability

of [η^5-C_5H_3-1,3-$(CMe_2Ph)_2$]$TiCl_3$ (**34**)/MAO, which has *two* substituents that may be cyclometalated, seems to rule out this decomposition pathway. As a third possibility, cyclometalation of the EMe_3 substituent (E = Si, **32**, or E = C, **33**) itself might take place. Marks and coworkers reported that for cationic zirconocene species [(η^5-C_5H_4R)(η^5-$C_5H_4EMe_3$)ZrR']$^+$ this process occurs more easily for E = C than E = Si[44]. A similar trend in our systems could explain the greater stability of **32**/MAO relative to **33**/MAO in selective ethene trimerization.

The constant trimerization activity of **34**/MAO over extended run times (at least 2 h) suggests that the two CMe_2Ph groups alternately coordinate to the titanium center to effectively stabilize the active species. Competition between the loose pendant arene substituent and incoming ethene on the titanacyclopentane intermediate may result in a lower activity compared to the other derivatives.

The addition of a substituent on the cyclopentadienyl ring also affects the composition of the trimerization products formed. For the $SiMe_3$-substituted catalyst **32**/MAO, the 1-hexene content of the C_6 fraction rises to 99.9% (99.7% for **1**/MAO) and the 5-methylnon-1-ene content of the C_{10} fraction to 92% (85% for **1**/MAO). For the *tert*-butyl-substituted catalyst **33**/MAO these trends are similar (99.8% and 91%, respectively).



Scheme 1: Proposed dominant pathway for C_{10} product formation

Considering all the possibilities to form C_{10} products from ethene and 1-hexene via the proposed trimerization mechanism, it appears that one pathway is by far the most favorable. This is illustrated in Scheme 1, and proceeds through selective oxidative

coupling of ethene with 1-hexene to give a titanacylopentane with the *n*-butyl substituent on the β-carbon (**B**). This is followed by an insertion of ethene into the Ti-C bond at the unsubstituted side of the metallacycle, giving a β-(*n*-butyl)-substituted titanacycloheptane (**C**), and β-H abstraction from the unsubstituted β-carbon (**D**) to give, after reductive elimination, the 5-methylnon-1-ene. A similar pathway has been proposed for the cotrimerization of ethene and styrene with $[Cp^{R}TiMe_2]^+$ systems to afford, predominantly, 6-phenyl-1-hexene (due to the preferred 2,1-insertion of styrene)[45]. The similar product distribution within the C_{10} fractions observed for the $SiMe_3$ (**32**) and CMe_3 (**33**) substituted catalysts suggests that the selectivity of the cotrimerization is mainly controlled by the steric properties of the substituted cyclopentadienyl ligand rather than by its electronic properties.

5.5 Combining ligand effects

The investigation of the effect of single ligand variations on the catalytic ethene conversion with cyclopentadienyl-arene titanium species (variation in bridging group and substituents on the cyclopentadienyl moiety described above, and substituents on the aryl moiety described in Chapter 4) has resulted in the identification of specific features that appear to be advantageous to catalyst efficiency. When compared under standard conditions to the reference catalyst **1**/MAO, the catalyst with the $C[(CH_2)_5]$ bridging group (**30**) shows a 17% increase in C_6 productivity, and the catalyst with the $SiMe_3$-substituted cyclopentadienyl group (**32**) a 20% increase. Combining these features in the catalyst $\{\eta^5\text{-}(3\text{-}SiMe_3)C_5H_3C[(CH_2)_5]Ph\}TiCl_3$ (**35**)/MAO leads to a 57% increase in C_6 productivity relative to **1**/MAO (Table 4). This suggests that the effects of variations in bridging group and cyclopentadienyl substituent are roughly additive, with a slightly positive nonlinearity.

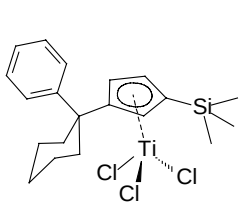
In contrast to the positive effect on C_6 productivity of substitution on the cyclopentadienyl group, the attachment of methyl subtituents on the aryl group was seen to lead to a decrease in C_6 productivity relative to **1**/MAO (for the catalyst with the $3,5\text{-}Me_2C_6H_3$ group (**2**) a reduction by 62%). Remarkably, the catalyst $[\eta^5\text{-}(3\text{-}SiMe_3)C_5H_3CMe_2\text{-}3,5\text{-}Me_2C_6H_3]TiCl_3$ (**36**)/MAO, combining Cp substitution with aryl substitution, turned out to be the most active catalyst of all (Table 4), with an increase in the rate of C_6 production by 92% relative to **1**/MAO and a very high selectivity for the combined trimerization products (99%). Aryl substitution in the *tert*-butyl-cyclopentadienyl derivatives $[\eta^5\text{-}(3\text{-}CMe_3)C_5H_3CMe_2Ar]TiCl_3$/MAO (Ar = Ph, **33**, $3,5\text{-}Me_2C_6H_3$, **37**) has no effect on initial ethene uptake rate, but significantly improves catalyst stability, as can be seen from the ethene uptake profile, affording a catalyst with comparable productivity over a 30 min run period as **1**/MAO (Table 4). The combination of substituents on the key positions (backbone, cyclopentadienyl and arene) can thus improve the three major parameters in the catalytic trimerization process (activity, selectivity and stability). The precise

interplay of steric and electronic effects is as yet unclear, and warrants further investigation.

Table 4: Catalytic ethene conversions with the [η^5-(3-R)$C_5H_4CX_2Ar$]$TiCl_3$/MAO catalyst systems (toluene solvent, 5 bar ethene, 30 °C, 15 µmol Ti, Al:Ti = 1000, 30 min reaction time)

Catalyst (R, X, Ar)	C_6 products [g] (wt%)	C_{10} products [g] (wt%)	PE [g] (wt%)	Productivity C_6 products[a]	Trimerization products [wt%]	Trimerization productivity[b]
1 (H, Me, Ph)	20.9 (83)	3.5 (14)	0.5 (1.8)	555	97	109.5
30 (H, $[CH_2]_5$, Ph)	24.4 (87)	2.9 (10)	0.6 (2.0)	650	97	124.5
35 ($SiMe_3$, $[CH_2]_5$, Ph)	33.9 (84)	5.2 (13)	1.2 (3.0)	905	97	176.5
2 (H, Me, 3,5-$Me_2C_6H_3$)	7.9 (93)	0.1 (4)	0.1 (1.3)	210	97	38.0
36 ($SiMe_3$, Me, 3,5-$Me_2C_6H_3$)	40.1 (84)	7.0 (15)	0.3 (0.6)	1070	99	211.0
37 (CMe_3, Me, 3,5-$Me_2C_6H_3$)	24.4 (91)	1.6 (6)	0.7 (2.8)	650	97	121.0

[a] in g C_6 product per mmole Ti, bar and h; [b] in mole olefinic bonds trimerized per mmole Ti and h



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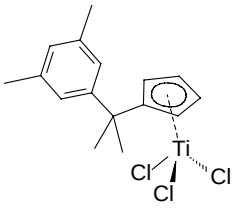

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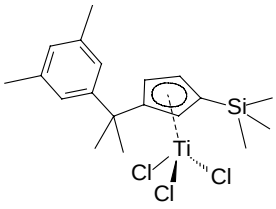

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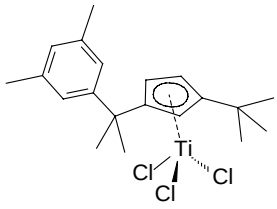

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5.6 Conclusions

We have shown that a wide range of titanium precatalysts of the type [η^5-C_5H_3R-(B)-Ar]$TiCl_3$ can be activated with MAO to give highly active and selective ethene trimerization catalysts. A summary of these results is listed in Table 5. The nature of the bridging moiety (B) between the cyclopentadienyl and the arene group is crucial for obtaining a good selectivity in 1-hexene production. Only disubstituted C_1-bridges afford highly selective and active ethene trimerization catalysts. Apparently, the conformational constraints imposed by the bridging unit are of major importance to catalyst performance. The introduction of additional substituents on the cyclopentadienyl moiety can influence both catalyst activity and stability. The introduction of a trimethylsilyl substituent is highly favorable for catalyst activity, whereas the addition of a second CMe_2Ph substituent greatly increases catalyst stability (albeit at the cost of a lower activity). Combining two ligand variations at a time shows in some cases a significant positive nonlinear additivity of the substituent effects on catalyst activity. In addition, steric effects can be employed to improve the

selectivity for formation of a single mono-methyl branched α-olefin product in the cotrimerization of ethene with 1-alkenes.

Table 5: Overview of trimerization activity and selectivity with [η^5-(3-R)C_5H_3-(B)-Ar]$TiCl_3$/MAO systems[a]

Precatalyst	R	B	Ar	Trimerization products [wt%]	Trimerization productivity[b]
1	H	CMe_2	Ph	97	109.5
24	H	CMe_2	4-MeC_6H_4	98	74.5
2	H	CMe_2	3,5-$Me_2C_6H_3$	97	38.0
26	H	CH_2	Ph	<51	-
27	H	$SiMe_2$	Ph	<43	-
28	H	CMe_2CH_2	Ph	86	5.5
29	H	CEt_2	Ph	95	92.0
30	H	C[$(CH_2)_5$]	Ph	97	124.5
31	H	$C=CH_2$	Ph	95	86.5
32	$SiMe_3$	CMe_2	Ph	96	129.5
33	CMe_3	CMe_2	Ph	94	72.5
34	CMe_2Ph	CMe_2	Ph	96	58.5
35	$SiMe_3$	C[$(CH_2)_5$]	Ph	97	176.5
36	$SiMe_3$	CMe_2	3,5-$Me_2C_6H_3$	99	211.0
37	CMe_3	CMe_2	3,5-$Me_2C_6H_3$	97	121.0

[a] toluene solvent, 5 bar ethene, 30 °C, 15 µmol Ti, Al:Ti = 1000, 30 min reaction time

[b] in mole olefinic bonds trimerized per mmole Ti and h

The catalyst precursor titanium complexes are readily synthesized, and ligand variations can be easily introduced. These titanium-based catalyst systems provide a well-defined, highly active and non-toxic alternative to the currently available chromium-based ethene trimerization catalysts.

5.7 Experimental Section

General considerations - All experiments were carried out under purified nitrogen atmosphere using standard Schlenk and glovebox techniques. Deuterated solvents (Aldrich, Acros) were either dried over Na/K alloy and vacuum transferred before use (C_6D_6) or degassed and dried on molecular sieves (Aldrich, 4Å). Cyclooctane (Aldrich) was distilled from sodium prior to use, and was used as internal standard in the catalytic ethene conversion experiments. Toluene (Aldrich, anhydrous, 99.8%) was passed over columns of Al_2O_3 (Fluka), BASF R3-11 supported Cu oxygen scavenger and molecular sieves (Aldrich,

4Å) under nitrogen atmosphere prior to use. Diethyl ether and THF (Aldrich, anhydrous) were dried over Al_2O_3 (Fluka) and the other solvents (Aldrich) were dried over molecular sieves (Aldrich, 4Å) under nitrogen atmosphere before use. Ethene (AGA polymer grade) was passed over BASF R3-11 supported Cu oxygen scavenger and molecular sieves (Aldrich, 4Å). - NMR spectra were recorded on Varian Gemini 200/300 and Unity 500 spectrometers in NMR tubes equipped with a teflon Young valve. The ^{1}H NMR spectra were referenced to resonances of residual protons in the deuterated solvents (δ = 7.15 ppm for C_6D_6, δ = 7.24 ppm for $CDCl_3$). The ^{13}C NMR spectra were referenced to the carbon resonances of the deuterated solvent (δ = 128 ppm for C_6D_6). Chemical shifts (δ) are given relative to tetramethylsilane (downfield shifts are positive). GC analyses were performed on a HP 6890 instrument equipped with a HP-1 dimethylpolysiloxane column (19095 Z-123). GC/MS analyses were conducted using a HP 5973 mass-selective detector attached to a HP 6890 GC instrument. Elemental analyses were performed at the Microanalytical Department of the University of Groningen. Given values are the average of at least two independent determinations. - The compounds (η^5-$C_5H_4CH_2Ph$)$TiCl_3$ (**26**)[26], (η^5-$C_5H_4SiMe_2Ph$)$TiCl_3$ (**27**)[35], (η^5-$C_5H_4CMe_2CH_2Ph$)$TiCl_3$ (**28**)[35], [$C_5H_4C(=CH_2)Ph$]Li[46], and 3-α,α-dimethylbenzyl-6,6-dimethylfulvene[47] were prepared according to published procedures. The 6,6-diethylfulvene was prepared from cyclopentadiene and 3-pentanone analogously to the procedure described for 6,6-pentamethylenefulvene[48], and 3-*tert*-butyl-6,6-dimethylfulvene was prepared from *tert*-butylcyclopentadiene and acetone analogously to 3-α,α-dimethylbenzyl-6,6-dimethylfulvene[47]. A toluene solution of MAO (9.8 wt% Al, Akzo Nobel Chemicals) was used as received.

Preparation of $C_5H_4(SiMe_3)CEt_2Ph$ - To a solution of 4.85 g (58 mmol) PhLi in 200 ml of diethyl ether, cooled at -50 °C, 8.0 g (60 mmol) of 6,6-diethyl fulvene was added dropwise. The reaction mixture was allowed to warm to room temperature and was stirred for 3 hours. The yellow solution was then cooled with an ice bath and 7.6 ml (6.5 g, 60 mmol) of trimethylsilyl chloride was added dropwise. The mixture was allowed to warm to room temperature and stirred overnight. The reaction mixture was poured into 250 ml of ice water. The water layer was extracted with 2x 100 ml of light petroleum, after which the combined organic layers were rinsed with 200 ml of brine. The organic phase was dried on $MgSO_4$. After evaporating the low-boiling volatiles in vacuo, the residue was distilled using a Kugelrohr-apparatus. The product distilled at 110 °C at 0.5 mm Hg as a mixture of isomers. Yield: 9.21 g (32 mmol, 55%) - ^{1}H NMR (300 MHz, $CDCl_3$, main isomer): δ 7.28 (m, 4H, Ph *o*- and *m*-H), 7.18 (m, 1H, Ph *p*-H), 6.40 (m, 1H, Cp), 6.31 (s, 1H, Cp), 6.22 (m, 1H, Cp), 3.27 (s, 1H, Cp), 2.02 (m, 4H, α-CH_2), 0.72 (m, 6H, β-CH_3), 0.06 (s, 9H, $SiMe_3$)

Preparation of (η^5-$C_5H_4CEt_2Ph$)$TiCl_3$ (29) - To a solution of 6.30 g (22 mmol) of $C_5H_4(SiMe_3)CEt_2Ph$ in 40 ml of methylene chloride, cooled at -40 °C, 2.45 ml (4.2 g, 22 mmol) of $TiCl_4$ was added. The mixture was allowed to warm to room temperature and stirred overnight. The methylene chloride was removed in vacuo and the residue was stirred with 50 ml of pentane, which was subsequently pumped off. Extraction with methylene chloride and cooling to -60 °C afforded red brown crystals of the title compound. Yield: 5.63 g (15.3 mmol, 70%) - ^{1}H NMR (300 MHz, C_6D_6): δ 7.24 (d, $^3J_{HH}$ = 7.3 Hz, 2H, Ph *o*-H), 7.17 (t, $^3J_{HH}$ = 7.3 Hz, 2H, Ph *m*-H), 7.06 (t, $^3J_{HH}$ = 7.3 Hz, 1H, Ph *p*-H), 6.26 (ps. t, $^3J_{HH}$ = 2.8 Hz, 2H, Cp), 6.04 (ps. t, $^3J_{HH}$ = 2.8 Hz, 2H, Cp), 2.06 (m, 2H, α-CH_2), 1.86 (m, 2H, α-

CH_2), 0.51 (t, $^3J_{HH}$ = 7.3 Hz, 6H, β-CH_3) - ^{13}C NMR (75.4 MHz, C_6D_6): δ 154.8, 142.1 (Ph and Cp C *ipso*), 128.8 (Ph *o*-CH), 128.3 (Ph *m*-CH, overlap with solvent), 127.2 (Ph *p*-CH), 123.1, 121.8 (Cp CH), 48.6 (CEt_2 C *ipso*), 29.3 (α-CH_2), 8.5 (β-CH_3) - Anal. Calcd for $C_{16}H_{19}TiCl_3$: C, 52.57; H, 5.24; Ti, 13.10. Found: C, 52.75; H, 5.27; Ti, 12.99.

Preparation of $C_5H_4(SiMe_3)C[(CH_2)_5]Ph$ - To a solution of 4.00 g (48 mmol) PhLi in 200 ml of diethyl ether, cooled at -50 °C, 6.95 g (48 mmol) of 6,6-pentamethylenefulvene was added dropwise. The reaction mixture was allowed to warm to room temperature and was stirred for 3 hours. Subsequently the yellow solution was cooled with an ice bath and 6.4 ml (5.5 g, 51 mmol) of trimethylsilyl chloride was added dropwise. The mixture was allowed to warm to room temperature and stirred overnight. The reaction mixture was poured into 250 ml of ice water. The water layer was extracted with 2x 100 ml of light petroleum, after which the combined organic layers were rinsed with 200 ml of brine. The organic phase was dried on $MgSO_4$. After evaporating the low-boiling volatiles in vacuo, the residue was distilled using a Kugelrohr-apparatus. The product distilled at 165 °C at 0.4 torr as a mixture of isomers. Yield: 8.96 g (30 mmol, 63%) - ^{1}H NMR (300 MHz, $CDCl_3$, main isomer): δ 7.40 (m, 2H, Ph *o*-H), 7.33 (m, 2H, Ph *m*-H), 7.15 (m, 1H, Ph *p*-H), 6.43 (m, 2H, Cp), 6.15 (s, 1H, Cp), 3.27 (s, 1H, Cp), 2.17 (m, 4H, α-CH_2), 1.65-1.40 (m, 6H, β- and γ-CH_2), -0.03 (s, 9H, $SiMe_3$)

Preparation of {η^5-$C_5H_4C[(CH_2)_5]Ph$}$TiCl_3$ (30) - Titanium chloride (1.4 ml, 2.4 g, 12.7 mmol) was added to a solution of 3.70 g (12.5 mmol) of $C_5H_4(SiMe_3)C[(CH_2)_5]Ph$ in 40 ml of methylene chloride, cooled at -40 °C. The reaction mixture was allowed to warm to room temperature and was stirred overnight. The methylene chloride was removed in vacuo and the residue was stirred with 30 ml of pentane, which was subsequently pumped off. The residue was extracted with methylene chloride. Crystallization from a 1:1 mixture of CH_2Cl_2/pentane afforded red-brown crystals of the title compound in 78% yield (3.68 g, 9.7 mmol). - ^{1}H NMR (300 MHz, C_6D_6): δ 7.16-7.06 (m, 4H, Ph *o*- and *m*-H), 7.01 (m, 1H, Ph *p*-H), 6.31 (ps. t, $^3J_{HH}$ = 2.8 Hz, 2H, Cp), 5.97 (ps. t, $^3J_{HH}$ = 2.8 Hz, 2H, Cp), 2.45 (d, $^2J_{HH}$ = 13.2 Hz, 2H, α-CH_2 (eq)), 1.88 (m, 2H, α-CH_2 (ax)), 1.37 (br, 3H, β- and γ-CH_2), 1.25-1.05 (m, 3H, β- and γ-CH_2) - ^{13}C NMR (75.4 MHz, C_6D_6): δ 156.0, 142.1 (Ph and Cp C *ipso*), 129.2 (Ph *o*-CH), 127.9 (Ph *m*-CH), 126.8 (Ph *p*-CH), 123.2, 120.9 (Cp CH), 45.1 ($C[(CH_2)_5]$ C *ipso*), 35.8 (α-CH_2), 26.1 (γ-CH_2), 22.4 (β-CH_2) - Anal. Calcd for $C_{17}H_{19}TiCl_3$: C, 54.08; H, 5.07; Ti, 12.69. Found: C, 53.93; H, 4.90; Ti, 12.62.

Preparation of [η^5-$C_5H_4C(=CH_2)Ph$]$TiCl_3$ (31) - To a solution of 0.61 ml (1.06 g, 5.6 mmol) titanium chloride in 40 ml of methylene chloride, cooled at -50 °C, 1.80 g (5.6 mmol) $[C_5H_4C(=CH_2)Ph]Li$ was added. The reaction mixture was allowed to warm to room temperature and was stirred overnight. The volatiles were removed in vacuo and the green-black residue was stirred with 30 ml of pentane, which was subsequently pumped off. Extraction with pentane afforded small analytically pure amounts of the title compound as dark red crystals. Isolated yield: 0.25 g (0.8 mmol, 14%) - ^{1}H NMR (300 MHz, C_6D_6): δ 7.2-7.05 (m, 5H, Ph), 6.35 (ps. t, $^3J_{HH}$ = 2.7 Hz, 2H, Cp), 6.01 (ps. t, $^3J_{HH}$ = 2.7 Hz, 2H, Cp), 5.58 (s, 1H, =CH_2), 5.20 (s, 1H, =CH_2) - ^{13}C NMR (75.4 MHz, C_6D_6): δ 142.5, 139.7, 139.6 (Ph, Cp and C(=CH_2) C *ipso*), 128.8, 128.7, 128.5 (Ph CH), 123.4, 121.1, 120.5 (Cp CH and

=CH_2) - Anal. Calcd for $C_{13}H_{11}TiCl_3$: C, 48.57; H, 3.45; Ti, 14.90. Found: C, 48.71; H, 3.55; Ti, 14.78.

Preparation of $C_5H_3(SiMe_3)_2CMe_2Ph$ - To a solution of 2.25 g (11.8 mmol) $[C_5H_4CMe_2Ph]Li$ in 50 ml of diethyl ether and 20 ml of THF, cooled in ice water, 1.5 ml (1.3 g, 11.9 mmol) Me_3SiCl was added dropwise. The mixture was allowed to warm to room temperature and was stirred overnight. The yellow solution was cooled in ice water and 4.8 ml (12 mmol) of a 2.5M *n*-BuLi solution in hexanes was added. After warming up to room temperature the mixture was stirred for 4 hours. The white suspension was cooled in ice water and 1.6 ml (1.4 g, 12.7 mmol) Me_3SiCl was added dropwise. The mixture was allowed to warm to room temperature and stirred overnight. The yellow suspension was poured into 125 ml ice water. The water layer was extracted with 50 ml of light petroleum and the combined organic layers were dried on $MgSO_4$. After evaporation of low-boiling volatiles, the residue was distilled using a Kugelrohr-apparatus. The product distilled at 115 °C at 0.8 Torr. Yield: 2.87 g (8.7 mmol, 74%) - ^{1}H NMR (200 MHz, $CDCl_3$): δ 7.4-7.1 (m, 5H, Ph), 6.40 (d, $^3J_{HH}$ = 2.2 Hz, 2H, Cp), 6.20 (t, $^3J_{HH}$ = 2.1 Hz, 1H, Cp), 1.53 (s, 6H, CMe_2), -0.03 (s, 18H, $SiMe_3$)

Preparation of [η^5-(3-$SiMe_3$)$C_5H_3CMe_2Ph$]$TiCl_3$ (32) - To a solution of 0.92 ml (1.6 g, 8.4 mmol) $TiCl_4$ in 50 ml of methylene chloride, cooled at -50 °C, 2.75 g (8.4 mmol) of $C_5H_3(SiMe_3)_2CMe_2Ph$ was added. The reaction mixture was allowed to warm to room temperature and was stirred overnight. The volatiles were removed in vacuo and the residue was stirred with 15 ml of pentane, which was subsequently pumped off. Extraction with methylene chloride and cooling to -60 °C afforded 2.76 g (6.7 mmol, 80%) of the title compound. - ^{1}H NMR (300 MHz, C_6D_6): δ 7.1-6.85 (m, 6H, Ph and Cp), 6.57 (m, 1H, Cp), 6.53 (m, 1H, Cp), 1.63 (s, 6H, CMe_2), 0.12 (s, 9H, $SiMe_3$) - ^{13}C NMR (75.4 MHz, C_6D_6): δ 158.5, 148.5, 144.1 (Ph and Cp C *ipso*), 128.7, 128.6, 126.7, 126.1, 124.6 (Ph and Cp CH), 41.2 (CMe_2 C *ipso*), 29.3, 29.0 (CMe_2), -0.8 ($SiMe_3$) - Anal. Calcd for $C_{17}H_{23}SiTiCl_3$: C, 49.84; H, 5.66; Ti, 11.69. Found: C, 49.70; H, 5.68; Ti, 11.59.

Preparation of $[C_5H_3(CMe_3)CMe_2Ph]Li$ - To a solution of 3.80 g (45 mmol) phenyl lithium in 60 ml of diethyl ether, cooled at -40 °C, 7.4 g (46 mmol) 3-*tert*-butyl-6,6-dimethylfulvene was added. The reaction mixture was allowed to warm to room temperature and was stirred overnight. The volatiles were removed in vacuo. The yellow oil was suspended in 40 ml of hexane and was refluxed for 4 hours. The resulting off-white solid was filtered off and repeatedly rinsed with pentane to afford 5.50 g (22 mmol, 49%) of product. - ^{1}H NMR (300 MHz, C_6D_6/THF-d_8): δ 7.53 (d, $^3J_{HH}$ = 7.0 Hz, 2H, Ph *o*-H), 7.13 (t, $^3J_{HH}$ = 7.3 Hz, 2H, Ph *m*-H), 6.98 (m, 1H, Ph *p*-H), 5.85 (m, 2H, Cp), 5.79 (m, 1H, Cp), 1.81 (s, 6H, CMe_2), 1.45 (s, 9H, CMe_3)

Preparation of [η^5-(3-CMe_3)$C_5H_3CMe_2Ph$]$TiCl_3$ (33) - To a solution of 1.47 g (6.0 mmol) of $[C_5H_4(CMe_3)CMe_2Ph]Li$ in 30 ml of methylene chloride, cooled at -20 °C, 0.70 ml (1.2 g, 6.3 mmol) $TiCl_4$ was added dropwise. The red brown solution was allowed to warm to room temperature and was stirred overnight. The solvent was removed in vacuo and the residue was stirred with 20 ml of pentane, which was subsequently pumped off. Extraction with toluene afforded a brown oil that could not be crystallized from either

pentane, hexane, toluene or methylene chloride. The oil was repeatedly rinsed with cold pentane to give 1.98 g (5.0 mmol, 83%) of product (about 95% purity as indicated by NMR spectroscopy). - ^{1}H NMR (300 MHz, C_6D_6): δ 7.1-7.0 (m, 3H, Ph *m*- and *p*-H), 6.87 (d, $^{3}J_{HH}$ = 7.0 Hz, 2H, Ph *o*-H), 6.60 (ps. t, $^{3}J_{HH}$ = 2.4 Hz, 1H, Cp), 6.40 (ps. t, $^{3}J_{HH}$ = 3.3 Hz, 1H, Cp), 6.29 (ps. t, $^{3}J_{HH}$ = 2.9 Hz, 1H, Cp), 1.64 (s, 3H, CMe_2), 1.63 (s, 3H, CMe_2), 1.04 (s, 9H, CMe_3) - ^{13}C NMR (75.4 MHz, C_6D_6): δ 157.5, 156.1, 148.8 (Ph and Cp C *ipso*), 128.6, 126.6, 126.1 (Ph CH), 120.5, 120.0, 119.6 (Cp CH), 41.6 (CMe_2 C *ipso*), 34.7 (CMe_3 C *ipso*), 30.4 (CMe_3), 28.9, 28.7 (CMe_2)

Preparation of [C_5H_3-1,3-($CMe_2Ph)_2$]Li - To a suspension of 2.28 g (27.1 mmol) PhLi in 50 ml of *n*-hexane 6.14 g (27.4 mmol) of 3-α,α-dimethylbenzyl-6,6-dimethylfulvene was added. The mixture was refluxed for 5 hours. The precipitate was poured onto a glass frit and rinsed with 2x 20 ml of pentane. Drying in vacuo yielded 4.18 g (13.6 mmol, 50%) of an off-white solid. - ^{1}H NMR (300 MHz, C_6D_6/THF-d_8): δ 7.55 (d, $^{3}J_{HH}$ = 8.2 Hz, 4H, Ph *o*-H), 7.16 (m, 4H, Ph *m*-H), 7.01 (m, 2H, Ph *p*-H), 5.87 (m, 1H, Cp), 5.83 (m, 2H, Cp), 1.79 (s, 12H, CMe_2) - ^{13}C NMR (75.4 MHz, C_6D_6/THF-d_8): δ 154.9, 129.0 (Ph and Cp C *ipso*), 127.8, 126.7, 124.7 (Ph CH), 100.8, 99.8 (Cp CH), 39.8 (CMe_2 C *ipso*), 32.5 (CMe_2)

Preparation of [η^5-C_5H_3-1,3-($CMe_2Ph)_2$]$TiCl_3$ (34) - To a solution of 1.31 g (4.2 mmol) of [C_5H_3-1,3-($CMe_2Ph)_2$]Li in 30 ml of methylene chloride, cooled at -40 °C, 0.47 ml (0.8 g, 4.2 mmol) $TiCl_4$ was added dropwise. The dark brown solution was allowed to warm to room temperature and was stirred overnight. The solvent was removed in vacuo and the residue was stirred with 40 ml of pentane, which was subsequently pumped off. The residue was extracted with 50 ml of toluene, which was replaced by a 1:1 mixture of methylene chloride/pentane (30 ml in total). Cooling to -40 °C afforded 0.22 g (0.5 mmol, 12%) of analytically pure **34**. - ^{1}H NMR (300 MHz, C_6D_6): δ 6.98 (m, 2H, Ph *p*-H), 6.96 (m, 4H, Ph *m*- or *o*-H), 6.70 (m, 4H, Ph *m*- or *o*-H), 6.50 (m, 1H, Cp), 6.40 (d, $^{3}J_{HH}$ = 2.6 Hz, 2H, Cp), 1.60 (s, 6H, CMe_2), 1.54 (s, 6H, CMe_2) - ^{13}C NMR (75.4 MHz, C_6D_6): δ 156.2, 148.8 (Ph and Cp C *ipso*), 128.4, 126.5, 126.0 (Ph CH), 121.5, 120.5 (Cp CH), 41.7 (CMe_2 C *ipso*), 28.5, 28.4 (CMe_2) - Anal. Calcd for $C_{23}H_{25}TiCl_3$: C, 60.62; H, 5.53. Found: C, 60.16; H, 5.56.

Preparation of $C_5H_3(SiMe_3)_2C[(CH_2)_5]Ph$ - To a solution of 1.67 g (7.3 mmol) {$C_5H_4C[(CH_2)_5]Ph$}Li in 70 ml of diethyl ether, cooled with ice water, 0.8 ml (0.7 g, 6.4 mmol) trimethylsilyl chloride was added dropwise. The reaction mixture was allowed to warm to room temperature and was stirred overnight. The white suspension was cooled to -30 °C and 7.3 mmol of a 2.5M solution of *n*-BuLi in hexanes was added dropwise. After stirring for 3 hours at ambient temperature, the reaction vessel was placed in ice water and 0.9 ml (0.8 g, 7.4 mmol) trimethylsilyl chloride was added. The reaction mixture was allowed to warm to room temperature and was stirred overnight. The mixture was poured into 100 ml of ice water. The water layer was extracted twice with 50 ml portions of light petroleum, and the combined organic layers were dried over $MgSO_4$. Kugelrohr-distillation at 160 °C and 0.4 Torr yielded 1.28 g (3.5 mmol, 55%) of the title compound - ^{1}H NMR (200 MHz, $CDCl_3$): δ 7.45-7.1 (m, 5H, Ph), 6.50 (m, 1H, Cp), 6.39 (m, 1H, Cp), 6.18 (m, 1H, Cp), 2.2 (m, 4H, α-CH_2), 1.55 (m, 6H, β- and γ-CH_2), -0.07 (s, 18H, $SiMe_3$)

Preparation of {η^5-(3-SiMe$_3$)C$_5$H$_3$C[(CH$_2$)$_5$]Ph}TiCl$_3$ (35) - To a solution of 0.34 ml (0.6 g, 3.2 mmol) titanium chloride in 40 ml of methylene chloride, cooled at -40 °C, 1.20 g (3.3 mmol) of $C_5H_3(SiMe_3)_2C[(CH_2)_5]Ph$ was added dropwise. The reaction mixture was allowed to warm to room temperature and was stirred overnight. The volatiles were removed in vacuo. Extraction with methylene chloride yielded red-brown crystals. Yield: 0.68 g (1.5 mmol, 47%). - ^{1}H NMR (300 MHz, C_6D_6): δ 7.13 (m, 4H, Ph *o*- and *m*-H), 7.01 (m, 1H, Cp), 6.93 (m, 1H, Ph *p*-H), 6.45 (m, 2H, Cp), 2.54 (m, 2H, α-CH_2 (eq)), 2.07, 1.86 (m, 1H, α-CH_2 (ax)), 1.4 (br, 3H, β- and γ-CH_2), 1.15 (br, 3H, β- and γ-CH_2), 0.13 (s, 9H, $SiMe_3$) - ^{13}C NMR (75.4 MHz, C_6D_6): δ 160.3, 143.6, 142.2 (Ph and Cp C *ipso*), 129.1, 128.7, 126.8, 126.7, 123.7 (Ph and Cp CH), 45.4 (C[$(CH_2)_5$] C *ipso*), 36.6, 35.7 (α-CH_2), 26.1 (γ-CH_2), 22.4 (β-CH_2), -0.8 ($SiMe_3$) - Anal. Calcd for $C_{20}H_{27}SiTiCl_3$: C, 53.41; H, 6.05; Ti, 10.65. Found: C, 52.83; H, 6.08; Ti, 10.52.

Preparation of C$_5$H$_3$(SiMe$_3$)$_2$CMe$_2$-3,5-Me$_2$C$_6$H$_3$ - To a solution of 1.15 g (5.3 mmol) $[C_5H_4CMe_2$-3,5-$Me_2C_6H_3]$Li in 50 ml of diethyl ether, cooled with ice water, 0.7 ml (0.6 g, 5.5 mmol) trimethylsilyl chloride was added dropwise. The reaction mixture was allowed to warm to room temperature and was stirred overnight. The white suspension was cooled to -30 °C and 5.4 mmol of a 2.5M solution of *n*-BuLi in hexanes was added dropwise. After stirring for 3 hours at ambient temperature, the reaction vessel was placed in ice water and 0.8 ml (0.7 g, 6.4 mmol) trimethylsilyl chloride was added. The reaction mixture was allowed to warm up to room temperature and was stirred overnight. The mixture was poured into 100 ml of ice water. The water layer was extracted twice with 50 ml portions of light petroleum, and the combined organic layers were dried over $MgSO_4$. Kugelrohr-distillation at 160 °C and 0.4 Torr yielded 1.26 g (3.5 mmol, 66%) of the title compound - ^{1}H NMR (200 MHz, $CDCl_3$): δ 6.90 (s, 2H, Ar *o*-H), 6.78 (s, 1H, Ar *p*-H), 6.37 (m, 2H, Cp), 6.19 (m, 1H, Cp), 2.24 (s, 6H, ArMe), 1.51 (s, 6H, CMe_2), -0.05 (s, 18H, $SiMe_3$)

Preparation of [η^5-(3-SiMe$_3$)C$_5$H$_3$CMe$_2$-3,5-Me$_2$C$_6$H$_3$]TiCl$_3$ (36) - To a solution of 0.35 ml (0.6 g, 3.2 mmol) titanium chloride in 40 ml of methylene chloride, cooled at -40 °C, 1.18 g (3.3 mmol) of $C_5H_3(SiMe_3)_2CMe_2$-3,5-$Me_2C_6H_3$ was added dropwise. The reaction mixture was allowed to warm to room temperature and was stirred overnight. The volatiles were removed in vacuo. Extraction with pentane yielded 1.02 g (2.3 mmol, 72%) of light brown crystals. - ^{1}H NMR (300 MHz, C_6D_6): δ 6.96 (m, 1H, Cp), 6.69 (s, 2H, Ar *o*-H), 6.64 (m, 2H, Cp and Ar *p*-H), 6.55 (m, 1H, Cp), 2.08 (s, 6H, ArMe), 1.70 (s, 6H, CMe_2), 0.13 (s, 9H, $SiMe_3$) - ^{13}C NMR (75.4 MHz, C_6D_6): δ 159.1, 148.5, 144.1 (Ar and Cp C *ipso*), 137.9 (Ar *m*-C *ipso*), 128.8, 128.4, 127.8, 124.7, 124.1 (Ar and Cp CH), 41.2 (CMe_2 C *ipso*), 29.3, 29.2 (CMe_2), 21.5 (ArMe), -0.9 ($SiMe_3$) - Anal. Calcd for $C_{19}H_{27}SiTiCl_3$: C, 52.13; H, 6.22; Ti, 10.94. Found: C, 51.72; H, 6.24; Ti, 10.76.

Preparation of [C$_5$H$_4$(CMe$_3$)CMe$_2$-3,5-Me$_2$C$_6$H$_3$]Li - A solution of 1.88 g (17 mmol) 3,5-dimethylphenyl lithium in 40 ml of diethyl ether was cooled to -40 °C. An equimolar amount of 3-*tert*-butyl-6,6-dimethylfulvene (2.7 g) was added. The reaction mixture was allowed to warm to room temperature and was stirred overnight. Removing the solvent in vacuo gave a yellow oil which solidified in refluxing hexane. The solid was repeatedly rinsed with pentane to yield 2.35 g (8.6 mmol, 51%) of the title compound. - ^{1}H NMR (300

MHz, C_6D_6/THF-d_8): δ 7.17 (s, 2H, Ar *o*-H), 6.63 (s, 1H, Ar *p*-H), 5.81, 5.77, 5.71 (m, 1H each, Cp), 2.13 (s, 6H, ArMe), 1.77 (s, 6H, CMe_2), 1.40 (s, 9H, CMe_3)

Preparation of [η^5-(3-CMe_3)$C_5H_3CMe_2$-3,5-$Me_2C_6H_3$]$TiCl_3$ (37) - To a solution of 1.54 g (5.6 mmol) of [C_5H_4(CMe_3)CMe_2-3,5-$Me_2C_6H_3$]Li in 30 ml of methylene chloride, cooled at -20 °C, 0.65 ml (1.1 g, 5.8 mmol) titanium tetrachloride was added dropwise. The mixture was allowed to warm to room temperature and was stirred overnight. Removing the volatiles, and extraction with toluene afforded a brown oil. Repeated rinsing with cold pentane afforded 2.06 g (4.9 mmol, 88%) of the oil, which was 95% pure as seen by NMR spectroscopy. - ^{1}H NMR (300 MHz, C_6D_6): δ 6.7-6.5 (m, 2H, Ar *p*-H and Cp), 6.63 (s, 2H, Ar *o*-H), 6.43 (t, $^3J_{HH}$ = 2.9 Hz, 1H, Cp), 6.29 (t, $^3J_{HH}$ = 2.9 Hz, 1H, Cp), 2.09 (s, 6H, ArMe), 1.70 (s, 3H, CMe_2), 1.69 (s, 3H, CMe_2), 1.05 (s, 9H, CMe_3) - ^{13}C NMR (75.4 MHz, C_6D_6): δ 157.3, 156.5, 149.0 (Ar and Cp C *ipso*), 137.8 (Ar *m*-C *ipso*), 124.6 (Ar *p*-CH), 124.1 (Ar *o*-CH), 120.6, 120.1, 119.5 (Cp CH), 41.7 (CMe_2 C *ipso*), 34.7 (CMe_3 C *ipso*), 30.4 (CMe_3), 29.0, 28.9 (CMe_2), 21.5 (ArMe)

General procedure for the catalytic ethene conversions - A stainless steel 1L autoclave (Medimex), fully temperature and pressure controlled and equipped with solvent and catalyst injection systems, was preheated in vacuo for 45 min at 100 °C prior to use. The reactor was cooled to the desired temperature, charged with 200 ml of toluene, and pressurized with ethene. After equilibrating for 15 min, the appropriate amount of MAO/toluene was injected, together with 25 ml of toluene. Subsequently, a mixture of 2.50 g cyclooctane (internal standard) and 1.0 ml of a 15 mM stock solution of the titanium halide complex in toluene was injected, together with 25 ml of toluene, to start the reaction. During the reaction the ethene pressure was kept constant to within 0.1 bar of the initial pressure by replenishing flow. The run was ended by adding an aliquot of ethanol, and the reactor was vented. Remaining residual MAO was destroyed by adding further ethanol, and samples of the reaction mixture were taken to analyze and quantify the soluble components by GC and GC/MS. The polymer was stirred for 1 h in acidified ethanol, repeatedly rinsed with ethanol on a glass frit, and dried in vacuo at 70 °C overnight.

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